*Canadian Mineralogist,*
Vol. 12, pp. 26-32 (1973)

# THE STABILITY OF GASPEITE IN INERT ATMOSPHERES AND IN AIR

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## ABSTRACT

The rate of dissociation and the degree of stability of magnesian gaspeite in air and in inert gases (nitrogen and argon) were studied over the temperature range 20 to 600°C by TGA and DTA. In the temperature range under consideration, the solid end-products are NiO and MgO. The rate of dissociation of gaspeite is practically independent of the initial amount of material and is mainly a function of the temperature, of the composition of the gaseous medium in which the reaction takes place, and of the grain size. Variations of gaspeite concentration are of minor importance. The reaction is approximately of the first order with respect to the amount of undecomposed carbonate. The activation energies, calculated from 46 low- to high-temperature experiments and extrapolated down to 110°C, vary between 23.1 and 34.2 kcal mole$^{-1}$. The variation of the activation energies with temperature in the low temperature range was assumed to be linear. The instability of magnesian gaspeite in air at 20°C (room temperature) is established.

The metastability of gaspeite at room temperature can be explained by the formation of a film (thin layer) of NiO-MgO in the same way as Al is metastable in air due to a coating of $Al_2O_3$; it is more probable, however, that the persistence of gaspeite in a geological setting is due to its enclosure in surrounding rocks in which the local development of $CO_2$ pressure in the very small free space available is sufficient to suppress decomposition.

## INTRODUCTION

Gaspeite is an unusual mineral in space and time. As recently as 1965, Goldsmith & Northrop stated that normal nickel carbonate was unknown in nature. Isaacs (1963) found that natural nickel carbonate occurs as a hexahydrate (hellyerite, $NiCO_3 . 6H_2O$) and as a hydroxyhydrate (zaratite, $\sim NiCO_3 . 2Ni(OH)_2 . 4H_2O$). Calcites containing 0.83 and 0.65% Ni were reported by Maksimović (1952) and Maksimović & Stupar (1953). Chu-siang *et al.* (1964) identified a natural magnesium-nickel carbonate, called hoshiite (now discredited), having properties very similar to gaspeite from the Mount Albert area.

The Mount Albert gaspeite has been described in detail by Kohls & Rodda (1966) and Cimon (1966). The mineral occurs near Mount Albert, Lemieux Township, Quebec, as light emerald, zoned, crystalline rhombs ($\leq$0.6 mm in length) in a vein, 2.5 feet wide, in varicoloured to buff siliceous Silurian dolomite intruded by serpentinized plugs. Associated with the gaspeite are (Cr,Al) spinel, serpentine, millerite, nickeline, gersdorffite, polydymite, heazlewoodite, magnesite, and annabergite.

A detailed study of the rate of dissociation (*i.e.* the kinetics of decomposition) and the degree of thermal stability of gaspeite in air and in inert gases (nitrogen and argon) was undertaken over the temperature range 450-610°C in order to gain knowledge about the relative importance of grain size, temperature, degree of packing, gaseous medium used, and concentration of the reactant (gaspeite), and to explain certain characteristics that occur in the more general system Ni–O–C–S.

## EXPERIMENTAL METHOD

### *Starting material*

The material used in all experiments was obtained from Dr. R. Ledoux, Department of Geology, Université Laval, and consisted of natural gaspeite from the Mount Albert area, Gaspé Peninsula. Cimon (1966) observed the co-existence of two nickeliferous carbonate phases in the Mount Albert area. One phase is a nickeliferous magnesite whereas the other is a magnesian nickel carbonate. Both carbonates belong to the calcite group and have similar *d*-spacings. Treatment of these two carbonates in HCl indicated that the magnesium carbonate is soluble, whereas the nickeliferous carbonate is insoluble. After treatment with HCl, important changes were detected in the *x*-ray diffraction patterns (114 mm diam. Debye-Scherrer, filtered Cu radiation). For the untreated nickel carbonates, $d = 4.16$, 3.75, 3.525, 2.995, 2.717, 2.491, 2.303, 2.233, 1.930, 1.761, 1.688, 1.503, 1.487, and 1.401Å. When the carbonates were treated with HCl (1*N*), the *d*-spacings at 4.16, 3.75, 2.995, 2.491 and 2.233Å disappeared. The *d*-spacings given by the insoluble residual nickeliferous carbonate lie between those of $NiCO_3$ and $MgCO_3$ and are very close to data given by Langlès (1952) and Isaacs (1963). For comparison, the *d*-spacings of the nickel carbonates identified by Chu-siang *et al.* (1964), by Kohls & Rodda (1966) and those of $MgCO_3$ are given in Table 1. As pointed out by Kohls & Rodda (1966): "The similarity of the crystallographic data for magnesian gaspeite, for $MgCO_3$, and for $NiCO_3$, and the similar ionic size of nickel, magnesium, and iron suggest that all three have the same calcite-type structure." Wet chemical analysis of the insoluble nickel carbonate treated with HCl yielded 36.82% NiO, 14.83 MgO, 0.54 CaO, 40.25 $CO_2$, 0.17 MnO, 4.33 FeO, 0.98 $SiO_2$, 0.11 $H_2O^+$ and 0.34 $H_2O^-$; semi-quantitative optical spectrographic analysis revealed the following impurities: 0.01-0.1% Cr, Na, Co; 0.001-0.01% Al, Ba, Li, Sr; 0.001% Cu.

Adler & Kerr (1963a, 1963b) have published many infrared spectra of various carbonates but the spectrum of nickel carbonate is not included. Kohls & Rodda (1966) reported that infrared absorption occurs at 7.00, 11.42 and 13.32 microns for the gaspeite $(Ni_{0.49}Mg_{0.43}Fe_{0.08})CO_3$ studied. An infrared spectrum of nickel carbonate from Mount Albert was obtained with a Perkin-Elmer double-grating spectrometer Model 621, using a high-resolution monochromator. KBr pellets were prepared using 1.0 mg of finely-powdered mineral in 200 mg of KBr. The experimental method was similar to that described by Adler & Kerr (1963a, 1963b). The infrared spectra of the nickel carbonate of the Mount Albert area, before and after treatment with HCl, are shown in Figure 1. Before treatment with HCl, absorption bands were observed at 5.55, 6.99 ($\nu_3$), 9.90, 11.49 ($\nu_2$), 13.33 and 13.70 ($\nu_4$) microns, whereas, after treatment with HCl, they were at 5.55, 6.99 ($\nu_3$), 9.90, 11.49 ($\nu_2$) and 13.70 ($\nu_4$) microns. Typical spectra of the calcite depict three main absorption bands for the $CO_3$ molecule; these modes of vibration are designated as $\nu_2$, $\nu_3$ and $\nu_4$. One of the absorption bands of the doublet (13.33 and 13.70μ) disappears when the nickel carbonate is treated with HCl. This result indicates that one of the two nickel carbonate phases went into solution in HCl. The increase in intensity of the absorption band at 9.90μ, corresponding to the Si-O mode of vibration, represents an enrichment of the $SiO_2$ impurity in the insoluble nickel carbonate phase after treatment in HCl.

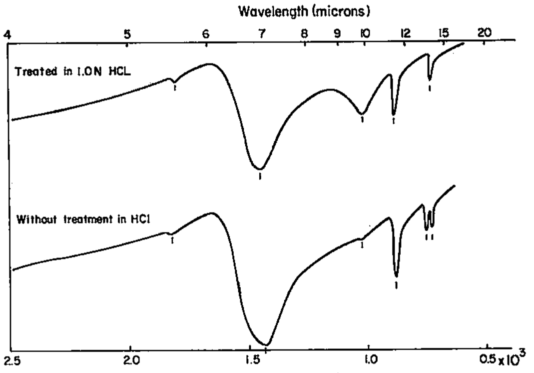

FIG. 1. Infrared spectra of magnesian nickel carbonate from the Mount Albert area. Absorbance increases downward.

A semi-quantitative microprobe analysis was conducted; many lines oriented in various directions were traversed on polished sections of the nickel carbonate of Mount Albert. The relative intensity distribution ($I/I_0$, expressed in %) was obtained, for Ni, Co, Mn, Mg and Ca. Concentrations of Co, Mn and Ca are, without exception, directly proportional to that of Ni, whereas that of Mg is always inversely proportional to that of Ni. The presence of a zoned texture, as observed under the microscope and in the microprobe, the enrichment in nickel and impoverishment in magnesium detected by chemical analyses after treatment with HCl, and the disappearance of one mode of vibration in infrared spectrometry after such treatment, are evidence supporting the co-existence of two phases of nickeliferous carbonates as indicated by Goldsmith & Northrop (1965). They observed the co-existence of two phases, one a nickeliferous magnesite and the other a magnesian nickel carbonate. If one considers that only $Ni^{2+}$, $Mg^{2+}$ and $Ca^{2+}$ enter into the chemical formula of the mineral, the composition of the insoluble nickel-rich phase is $Ni_{0.566}Mg_{0.423}Ca_{0.011}CO_3$; it is this phase that will be dealt with in detail in this paper.

TABLE 1. COMPARISON BETWEEN *d*-SPACINGS (Å) OF $NiCO_3$, $MgCO_3$, AND $(Ni,Mg,Ca)CO_3$

| $hk\bar{i}l$ | $10\bar{1}2$ | $10\bar{1}4$ | 0006 | $11\bar{2}1$ | $11\bar{2}3$ | $20\bar{2}2$ | $02\bar{2}4$ | $11\bar{2}6$ | $21\bar{3}1$ |
|---|---|---|---|---|---|---|---|---|---|
| $NiCO_3$ (Länglès 1952) | 3.504 | 2.704 | -- | 2.299 | 2.089 | 1.922 | 1.752 | 1.676 | 1.477 |
| $NiCO_3$ (Isaacs 1963) | 3.5077 | 2.7040 | -- | 2.3001 | 2.0828 | 1.9224 | 1.7511 | 1.678 | 1.4746 |
| Ni carbonate, Mt. Albert (insol. in HCl) | 3.525 | 2.730 | -- | 2.309 | 2.093 | 1.9305 | 1.7597 | 1.687 | 1.481 |
| Gaspeite (Kohls & Rodda 1966) | 3.543 | 2.741 | -- | 2.317 | 2.098 | 1.932 | 1.766 | 1.692 | 1.485 |
| Ni carbonate (Chu-siang et al. 1964) | -- | 2.7393 | -- | -- | 2.103 | -- | -- | 1.6979 | 1.4849 |
| $MgCO_3$ (PDF 8-479) | -- | 2.742 | 2.503 | 2.318 | 2.102 | 1.939 | 1.769 | 1.700 | 1.488 |

Under the polarizing microscope, the zoned equigranular crystals show imperfect uniaxial negative extinction figures. The refractive indices are $n_\varepsilon = 1.58$ and $n_\omega = 1.81$. A comparison of the optical and crystallographic data for the magnesian nickel carbonate with those for $MgCO_3$ and $NiCO_3$ (Graf 1961; Langlès 1952; Isaacs 1963) shows the remarkable similarity of magnesian gaspeite to these two compounds (Kohls & Rodda 1966). A comparison of the data obtained for nickeliferous magnesites (Chu-siang *et al.* 1964) and for the magnesian nickel carbonate suggests that they are a solid-solution series, the end members of which are $MgCO_3$ and $NiCO_3$.

### *Instrumentation*

The decomposition of gaspeite was studied using thermogravimetric (TGA) and differential thermal analyses (DTA). With the first method (TGA), two types of experiments were performed; one type consisted of measuring the variation of mass of the reactant (gaspeite) as a function of temperature at a rate of 160°C/min. and obtaining a thermogram, whereas the other type was a method of isothermal analysis. The thermobalance used was a Perkin-Elmer (Canada) Model TGS-1. Ancillary equipment consisted of a Perkin-Elmer (Canada) temperature controller, a Philips Model PM 8100 dual-pen flatback recorder, and an inert-gas circulator. Among other advantages, this system permits an exact measurement of the temperature, a great sensitivity, a rapid cooling rate, and the attainment of an almost instantaneous isothermal equilibrium. The accuracy of the measurements of the mass differences is of the order of 0.2% and the temperature is controlled with a precision of ± 1°C.

The differential thermal analyses were performed with a conventional Stanton (Model Standata — 658) DTA instrument consisting of two cells; one containing a reference material ($\alpha$–$Al_2O_3$) and the other, the solid reactant (sample). Ancillary equipment included a temperature programmer and a Fisher Scientific Model PSOIWGA Servowriter II two-pen recorder. Platinum *vs.* 87% platinum : 13% rhodium thermocouples were used for these experiments. The uncertainty in temperature is ± 2°C. The programmed rate of temperature rise was 10°C/min.; the mass of the sample varied between 200 and 400 mg.

### *Control of $P(CO_2)$ and $(O_2)$*

The experiments were conducted in free air (static) and in an inert gas at the ambient temperature. Intentionally, no CO or $CO_2$ was circulated through the system. Buffered experiments using another method were also conducted but the results are not included in this paper.

### *Identification of the end products*

All crystalline products were identified by *x*-ray diffraction using either a Guinier focusing camera with Fe$K\alpha_1$ radiation (30 kv, 10 ma) or a Debye-Scherrer camera with Cu$K\alpha$ or Fe$K\alpha$ radiation. In cases of uncertainty, infra-red scanning was performed on the solid end-products.

### *Procedure*

Except for the DTA experiments, the experimental procedure in use has its foundation in mass-difference analysis. The calculations are made using the ratio of the material dissociated at time $t$ to the total amount dissociated at infinite time ($t = \infty$). In practice, the time for complete dissociation can be considered as finite (*e.g.*, time at 99.3% or at 99.8% dissociation). Then the percentage of gaspeite dissociated was plotted against log time (Fig. 2).

The order $n$ was then obtained as shown in Table 2. From equation (3) in Table 2, the half life of the reacting species is a function of the order of the reaction and is inversely proportional to the power $(n - 1)$ of the initial concentration. This expression holds for any value of the order $n = 1$; $n$ may be an integer or a fraction, positive, negative or zero.

An order $n$ was assumed for the reaction and the rate constant $K_n$ calculated directly from the curve log $t$ against the percentage dissociated. Using individual values of $K_n$ in some cases and the averaged value of $K_n$ in others, the experimental curve was reproduced from theory. If the theoretical time obtained compared well with the experimental time obtained, the order was re-

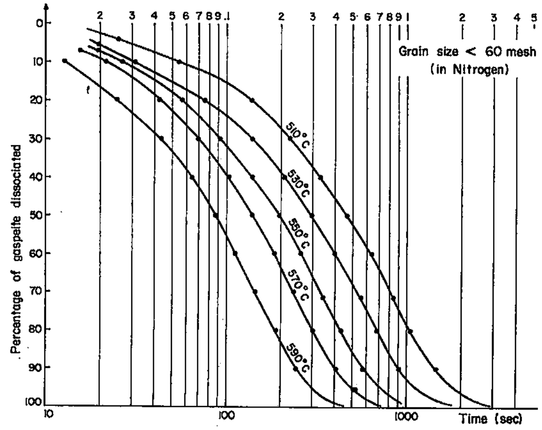

FIG. 2. Dissociation of gaspeite in nitrogen for 5 different isotherms.

tained. The rate constant, $K_n$, can also be obtained graphically by dividing the slope of a $\log_{10}(100 - x)$ against $t$ curve by $\log_{10}e$. It was established experimentally for gaspeite that the rate of dissociation is independent of the initial amount of reactant and that the order of the reaction is approximately one.

TABLE 2

The method of study is based on the rate of reaction of any order $n$, whose formula is

$$S = -\frac{dC}{dt} = K_n C^n \qquad (1)$$

where $S$=rate of the reaction, $C$=concentration of the reactant(s) in wt. %, $t$=time, $K_n$=rate constant (of order $n$), $n$=order.

Integrating equation (1):

$$K_n t = \frac{1}{n-1}\left(\frac{1}{C^{n-1}} - \frac{1}{C_0{}^{n-1}}\right) \quad \text{for } n \neq 1$$

$$\text{or} \quad K_n t = \frac{1}{(n-1)C_0{}^{n-1}} \left[\left(\frac{C_0}{C}\right)^{n-1} - 1\right] \qquad (2)$$

From equation (2), at $C=C_0/2$, the half life $t_{\frac{1}{2}}$ is given by

$$t_{\frac{1}{2}} = \left[\frac{2^{n-1} - 1}{(n-1)K_n}\right]\left[1/C_0{}^{n-1}\right] \qquad (3)$$

The equation for a first order reaction

$$-\frac{dC}{dt} = K_1 C \qquad (4)$$

on integration gives $\ln \frac{C}{C_0} = -K_1 t_1$ (5)

where $C$=wt. of non-reacted sample at time $t$, $C_0$= wt. of original sample at $t$=0, $C/C_0$=fraction of decomposed material.

For a first order reaction: $t_{\frac{1}{2}} = \ln_2 / K_1$ (6)
where $K_1$ is a constant.

The activation energy of the reaction can be calculated using the Arrhenius formula:

$$K_1 = K_0 e^{-E/RT}$$

where $K_0$=frequency factor or rate constant at infinite temperatures ($1/T$=0), $E$=activation energy, $R$=gas constant, $T$= temperature in degrees Kelvin.

Variation in concentration after time $t_1$:

$$\ln C_1 / C_0 = -K_1 t_1 \qquad (7)$$

after time $t_2$: $\ln C_2 / C_0 = -K_1 t_2$ (8)

To obtain almost complete dissociation (99.3%):

$$t_2 = -K_1{}^{-1} \ln C_2 / C_0 \qquad (9)$$

$$= \frac{-270}{\ln 0.9927} \ln C_2 / C_0$$

$$\text{or } t_2 = \frac{270}{-0.00732} \ln\left(\frac{1-0.17905}{0.18031}\right)$$

$$= \frac{270}{-0.00732} \ln\left(\frac{0.00126}{0.18031}\right) = \frac{270}{-0.00732}(-5.11600)$$

$$= 1.89 \times 10^5 \text{ days} \approx 520 \text{ years}$$

Integration of the equation for a first order reaction (equation 4, Table 2), yields equation (5) in Table 2. A linear plot of $\log C/C_0$ against $t$ will show that the reaction is first order.

## Experimental Results

Figures 2 and 3 show the results of some 10 thermobalance experiments on −60 mesh material. Seventy-five other experiments, some with −100 and others with −200 mesh material, were also performed in a nitrogen atmosphere and in air. Reaction temperatures ranged from 400–600°C for a nitrogen atmosphere, and 350–600°C for air. Similar experimental results and good reproducibility were obtained in both atmospheres.

### *Interpretation of results*

For a first order reaction, the half-life is given by (6) in Table 2. Knowing $K_1$ (which is a constant independent of the percentage of material reacted) and the percentage of material reacted, the corresponding time, $t$, may be calculated. That is, if the value of $K_1$ is correct, the experimental curve can be reproduced from theory; this was done. Once the rate constant $K_1$ is found, the activation energy of the reaction can be calculated by using the Arrhenius formula given in Table 2.

A plot of $\log_{10}K_1$ against $10^3/T$ gives a straight line, the slope of which is $E/4.576$. Because the order, rate constants, and temperatures are known, the activation energy can be calculated from low-temperature runs (400° and 450°C) for the reaction $(Ni_{0.566}Mg_{0.423}Ca_{0.11})CO_3 \rightarrow CO_2 +$

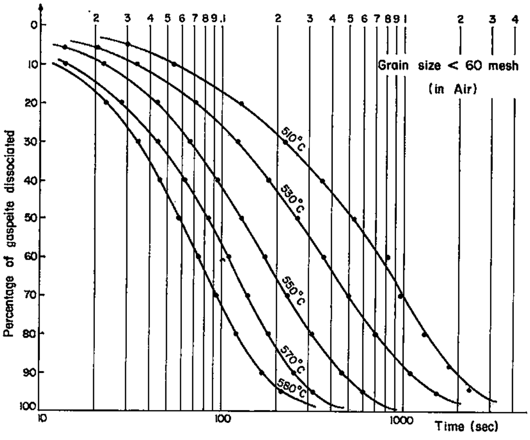

FIG. 3. Dissociation of gaspeite in air for 5 different isotherms.

(0.566 NiO + 0.423 MgO + 0.11 CaO) and extrapolated down to 100°C (*approximate instability limit of gaspeite in air*). Rate constants were found by extrapolation to lower temperatures. In the approximate temperature range 450° to 620°C, and for a grain size smaller than 60-mesh, the calculated activation energy was 23.9 kcal mole$^{-1}$ in a nitrogen atmosphere and 34.0 kcal mole$^{-1}$ in air. For smaller grain sizes (e.g., 200- and 300-mesh), the calculated activation energy was somewhat smaller. Figure 4 shows a plot of $\log_{10} K_1$ *vs* $10^3/T$ for some experiments performed in air and in a nitrogen atmosphere. The activation energies were calculated directly from this diagram.

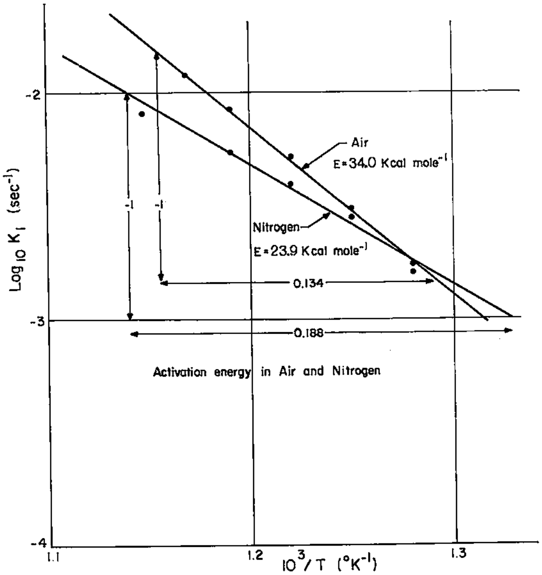

FIG. 4. Diagram of calculation of the activation energy for the decomposition of magnesian gaspeite in air and in nitrogen.

The dissociation of gaspeite is a direct reaction involving no intermediate products in the transition state. NiO is encountered as an end-product at all temperature ranges investigated; the other end-products are MgO, CaO (traces) and iron oxides (traces). The *x*-ray powder diffraction patterns of NiO are particularly in evidence. The time of nearly-complete dissociation (99.3%) obtained by calculation for a temperature of 20°C and in air is of the order of 520 years ($t^{1/2} = 2.6 \times 10^4$ days = 72 years) for a grain size smaller than 100-mesh, and at least twice as large for a size of approximately 60-mesh. This result was arrived at in the following way: after a time $t_1$, the variation in concentration is given by formula (7) in Table 2, and after time $t_2$, by formula (8). After 270 days ($t_1$) an original 0.42638-g. sample of gaspeite had lost 0.00131 g. (0.73%) at room temperature. As a gram molecular weight of $(Ni_{0.566}Mg_{0.423}Ca_{0.011})CO_3$ which is 104.1, would lose 44 g. of $CO_2$ at complete dissociation, the loss in weight of the original 0.42638-g. sample of gaspeite would be 0.18021 g. at complete dissociation (≃99.3%), that is:

$$\ln\left(1 - \frac{0.00131}{0.18031}\right) = (-K_1)\ (270) \text{ and thus } K_1 = -\ln 0.9927/270$$

Knowing $K_1$, one can calculate the time ($t_2$) required to obtain almost complete dissociation (99.3%) as shown in equation 9 in Table 2.

At 120°C, approximately 0.4% and 0.75% of the original magnesium gaspeite dissociated after 116 and 240 hours, respectively, and the average calculated value of $K_1$ is equal to $3.26 \times 10^{-5}$ hours$^{-1}$. The calculated half life ($t_{1/2}$) is then 2.43 years and after 17.1 years almost complete dissociation (99.2%) is attained. This means that, for all practical purposes, gaspeite is unstable in air and at the very most metastable in an inert atmosphere at room temperature. The experimental evidence (see Fig. 5) indicates that the rate of decomposition is slower in an inert atmosphere than in air. Large ideal crystals of gaspeite, approximately 5 to 8 cm across, may be geologically stable but such crystals have not yet been found in nature. Gaspeite heated in an oven at atmospheric pressure between 100° and 150°C for a few hours develops a coating of dull pistachio yellowish-green oxide indicating a preferential surface reaction. This thin coating of oxide(s) on gaspeite may act in exactly the same way as does $Al_2O_3$ on the surface of Al. The degree of packing of gaspeite in the containers, as well as variations of concentration of gaspeite when mixing it with inert components such as $Al_2O_3$, $SiO_2$, etc., does not change the order of the reaction.

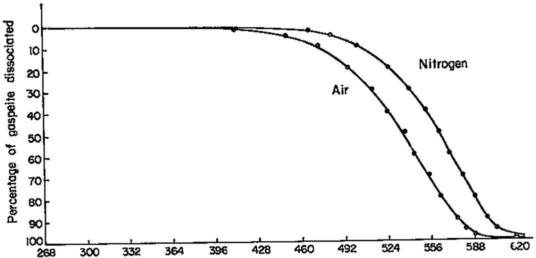

FIG. 5. Thermogram of magnesian gaspeite dissociated in an air and nitrogen gaseous medium.

In the low-temperature range (150° to 480°C), the rate of dissociation of gaspeite is faster in air than in nitrogen; actually, gaspeite is relatively stable in a nitrogen atmosphere below 380°C. This is not the case in air, where the dissociation is readily observed at 40°C (0.75% dissociated at 80°C after 400 hours). In the temperature range 500-580°C, the rate of dissociation is not very different in air from that in an atmosphere of nitrogen, but, above 580°C, the difference is more pronounced. This means that the gaseous medium alters the rate of the reaction and influences the speed of dissociation; thus at higher temperatures (roughly 570 to 600°C), gaspeite dissociates more slowly in air than in an inert atmosphere. The slower decomposition of the gaspeite in air above 570°C, as indicated by the thermogram, should also reflect the fact that almost all the gaspeite has already decomposed. One hypothesis that can explain this kinetic process is that the outward diffusion of large polar molecules, such as $CO_2$, is slowed by the surface layers of NiO (mainly), MgO and CaO that formed during carbonate decomposition. For a percentage of dissociated gaspeite smaller or equal to that corresponding to the half-life, gaspeite persists longer in air than in nitrogen in the high-temperature range; the opposite situation is encountered in the low-temperature range.

DTA curves were obtained for gaspeite at 1 atmosphere pressure (Fig. 7). The accuracy of the temperature is ± 2°C and that of the differential e.m.f. is ± 0.2µv; the programmed rate is 10°C/min. A typical DTA curve shows a single endothermic peak at 740°C. The endothermic reaction, which starts at 360 and is completed at 740°C, corresponds to the decomposition of the magnesian gaspeite into $CO_2$ and the Ni and Mg oxides; this suggests that either MgO and NiO form at the same temperature, or that the two endothermic peaks are unresolved and form a single fairly wide peak.

Isaacs (1963) conducted DTA experiments on several samples of synthetic $NiCO_3$ and observed only one endotherm at 345°C. Kohls & Rodda (1966) stated that the decomposition of magnesian gaspeite begins at 520°C and reaches an endothermic peak at 690°C. A DTA analysis of zaratite (Fig. 6) shows two endothermic peaks, the first corresponding to concurrent dehydration and loss of water of crystallization, and the second corresponding to carbonate decomposition into NiO. The thermal stability of the Mount Albert gaspeite is much greater than that of zaratite or synthetic $NiCO_3$.

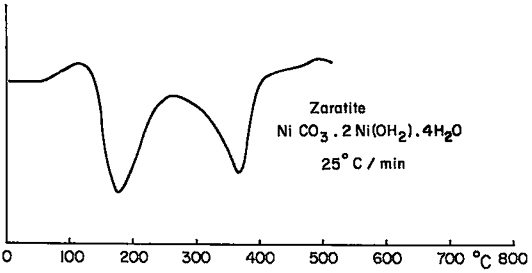

FIG. 6. Typical DTA curve of zaratite. The direction of endothermic reaction is downward.

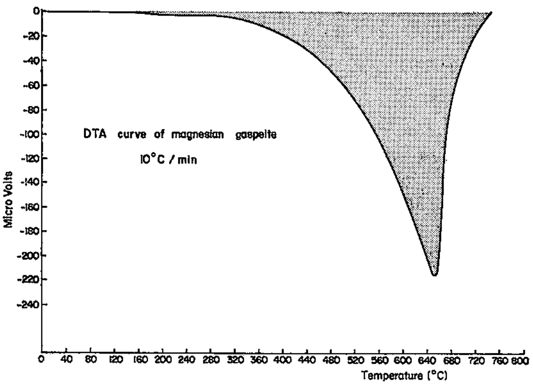

FIG. 7. DTA curve of gaspeite from the Mount Albert area. The direction of endothermic reaction is downward.

Attempts were made to calculate the variation in enthalpy or heat of reaction in a semi-quantitative fashion. The quantity of heat absorbed or released during a reaction is proportional to the area under the DTA curves obtained, the quantity of sample, the heat capacity of the sample, *etc.*. The instrument was calibrated using a standard FeO(OH) of trade mark Mapico, manufactured by Columbian Co. Ltd., Montreal, Canada, and by Mapico, Cities Service Co., U.S.A. The DTA curve shows an endothermic peak at 330°C and the temperature range of the peak extends from 230° to 360°C. The enthalpy of reaction of this dehydration is 16.0 kcal $mole^{-1}$ of $H_2O$ and the equivalent area under the curve is 3.334 volts C° per molecular weight. The equivalent area under the gaspeite decomposition curve (from 300 to 750°C) is 6.929 volts C° per molecular weight and so the enthalpy of reaction is the order of 33.2 kcal $mole^{-1}$ of $CO_2$ (Fig. 7). In all these experiments, the grain size was approximately 60 mesh.

## CONCLUSION

In the temperature range 20° to 600°C, the rate of dissociation of magnesian gaspeite is practically independent of the amount of admixed inert material and the degree of packing. Consistently similar results, obtained from experiments on systems with the gaspeite concentration, being varied by admixture of inert components and with differing degrees of packing, confirm this conclusion. In order of importance, the rate of dissociation is a function of the temperature of the gaseous atmosphere in which the reaction takes place, and of the grain size. A first-order equation was established for the reaction, and the activation energy was calculated for low-and medium-temperature reactions. No intermediate metastable dissociation products were detected.

For all practical purposes, magnesian gaspeite is metastable at room temperature and at 110°C in air. Up to a temperature of 350°C, gaspeite persists indefinitely in an inert atmosphere but would decompose very rapidly in air if it were it not for a thin surface layer composed of a mixture of NiO and MgO which inhibits the diffusion of $CO_2$ out of the crystal lattice. Thus, the smaller the grain size and the total binding energy, the greater the surface energy per unit volume favouring outward diffusion of large polar molecules.

Magnesian nickel carbonate is not found in great abundance in nature. The mineral occurs as fine grains, up to 0.5 mm in diameter, in veins and fractures in the Mount Albert area, and in an oxidized nickeliferous copper sulphide deposit in an arid region of central China (Chu-siang *et al.* 1964). Gaspeite is also known to occur at Pafuri Native Trust, Transvaal, Republic of South Africa, and at Kambalda, West Australia. The rarity of gaspeite in nature may be an indication of its instability under normal atmospheric conditions.

## ACKNOWLEDGEMENTS

Thanks are due to the National Research Council of Canada (grant no. 7070-110), to the Geological Survey of Canada (grant no. 30-68-1971) and to the Dept. of Physics of Université Laval for special funds for financially supporting this work.

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*Manuscript received June 1972, emended October 1972.*